PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-169132
(43)Date of publication of application : 20.06.2000

(51)Int.Cl. C01B 33/12
C08K 3/34
C09C 3/00
C09D 11/00
// A61K 7/00

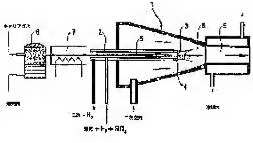
(21)Application number : 11-292911
(22)Date of filing : 14.10.1999

(71)Applicant : DEGUSSA HUELS AG
NIPPON AEROSIL CO LTD
(72)Inventor : MANGOLD HELMUT
OCHIAI MITSURU
GLAUM HOLGER DR
MUELLER ASTRID

(30)Priority
Priority number : 98 19847161 Priority date : 14.10.1998 Priority country : DE

(54) PYROLYTIC SILICON DIOXIDE DOPED WITH ALUMINUM OXIDE BY USING AEROSOL, ITS PRODUCTION, ITS USE AND ITS COMPOUNDED MATERIAL

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain silicon dioxide which can be easily dispersed in a polar solvent by doping silicon dioxide produced by a flame oxidation method or flame hydrolysis with aluminum oxide by using an aerosol.
SOLUTION: As for the doping component, a suspension liquid of aluminum salts or metal aluminum having 1×10-4 to 20 mass% is used to dope silicon dioxide with 1 to 10,000 ppm aluminum oxide. The BET specific surface area of the silicon dioxide after doped is 5 to 600 m2/g, and ≤100 g/100 g DBP absorption is obtd. In the production method, an aluminum chloride/water aerosol produced in an aerosol generator 6 is passed through a heating zone 7 by using a mild carrier gas flow such as air so as to convert the sol into gas and salt crystal aerosol. Then the sol is introduced into flame and uniformly mixed with the gas for flame oxidation or flame hydrolysis before the reaction and pyrolyzed in the flame to dope silicon dioxide with aluminum oxide. Thus, pyrolytic silicon dioxide suitable for an ink-jet material is obtd.



* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the use in the thermal decomposition method silicon dioxide (this silicon dioxide is dispersibility very easily in a polar medium) which doped the aluminum oxide using the aerosol, its process and its paper making especially ink jet paper, and an ink jet film. This invention relates to the use of further the for manufacture of low viscosity dispersion liquid, or for manufacture of high restoration dispersion liquid.
[0002]

[Description of the Prior Art]For example, extremely, the loading material of ******** is needed in order [which absorbs ink well in ink jet paper or an ink jet film, and holds the brightness of a color] to use it by pulp and paper industry.
[0003]In one distance of a special method, it is publicly known to dope a thermal decomposition method silicon dioxide in a flame (DE19650500A1, EP-A0850876). This method comprises the combination of high temperature flame hydrolysis and a pyrolysis. This doping method mixes beforehand a gas-like starting material (for example, a $SiCl_4$ gas and an $AlCl_3$ gas), is burned in a flame reactor together, and is distinguished from what is called a "KOHYUMUDO method" of the point from which the mixed oxide manufactured with the thermal decomposition method is obtained in that case.
[0004]The output manufactured using two different distance has the clearly different application characteristic.
[0005]
[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the pyrolysis manufacture silicon dioxide doped using the aerosol.
[0006]
[Means for Solving the Problem]In the doping method used by this invention, an aerosol is introduced into a flame, an oxide is manufactured by flame hydrolysis in it, and this aerosol contains a salt of a compound which should be doped in that case.
[0007]Now, if it is used as a start output for aerosols which should introduce an aluminium compound in which it was made to dissolve underwater, In order that a thermal decomposition method silicon dioxide which doped an aluminum oxide was obtained as an output, and this might be dispersibility very easily and might use it into ink jet paper and a film at a polar medium, for example, underwater, a dramatically suitable thing was found out.
[0008]Although a thermal decomposition method silicon dioxide which doped an aluminum oxide by this invention using an aerosol is obtained, This silicon dioxide is a silicon dioxide which a basic component manufactured with a thermal decomposition method using a flame oxidation style or flame hydrolysis, The ingredient is doped by a doping component to $1x10^{-4}$ and 20 mass %, In that case, doping quantity is 1-10000 ppm advantageously, and a doping component A salt or a salt mixture of aluminum, Or it is an aluminum salt compound, suspension of metallic aluminum, or its mixture, and BET surface area of a doped oxide is characterized by 5-600m^2/g and being the range of 40-100-m^2/g advantageously.
[0009]The silicon dioxide by this invention can have a DBP value below 100g/100g.
[0010]In order to provide a process of a thermal decomposition method silicon dioxide which doped an aluminum oxide by this invention using an aerosol and to use it for a thermal decomposition method silicon dioxide by a flame oxidation style or flame hydrolysis here, Introduce an aerosol into a flame, and before reacting an aerosol, it mixes with flame oxidation or a flame hydrolysis gaseous mixture to homogeneity, Subsequently, a thermal decomposition method silicon dioxide which the aerosol/gaseous mixture was made to react in a flame, and was produced and which doped an aluminum oxide, Dissociate from gas flow by a publicly known method, and an aerosol is manufactured using solution which contains a salt, a salt mixture, or the metal itself of aluminum in the dissolution, a suspended type, or its mixture in that case, In that case, it manufactures by spraying using 2 liquid nozzle of an aerosol, or is characterized by other

aerosol processes and manufacturing by aerosol generator advantageously using ultrasonic atomization.

[0011]Salts which can be used are $AlCl_3$, $aluminum_2(SO_4)_3$, and $aluminum(NO_3)_3$.

[0012]Flame hydrolysis manufacture of a thermal decomposition method oxide, i.e., for manufacture of a silicon dioxide (silica), Ur Mannes Ene cyclo PEDI Dell TEHINISHIEN It is publicly known from the 4th edition of HIEMI (Ullmanns Enzyklopaedie der technischen Chemie), the 21st volume, and 464 pages.

[0013]A thermal decomposition method silicon dioxide doped by this invention using an aerosol, Ink jet paper especially in pulp and paper industry and an ink jet film as a loading material, or other ink jet materials, For example, as a catalysis substance as a base material for manufacture of sail cloth, plastics, etc., As a lustering agent (CMP spreading) as a starting material for dispersion-liquid manufacture, As a loading material of polymer in electronic industry as a ceramic base material, As a starting material for glass, glass coating, or glass fiber manufacture, As adsorbent in cosmetic industry as an exfoliation auxiliary agent at a high temperature, An object for adjustment of the flowability of a fluid system as an additive in silicone and rubber industry, Use as filter ceramics in a fluorescent lamp in PET film paint in lacquer industry as an auxiliary agent in restrictions industry as a bulking agent or a starting material for manufacture of a filter is also obtained in dentistry industry as a flow auxiliary agent as thermal insulation for heat stabilization.

[0014]In this invention, the 0.01 to 100% compound of a silicon dioxide of this invention which is a loading material in ordinary use, or contains the mixture by other thermal decomposition method silicon dioxides, sedimentation method silicon dioxides, bentonites, or pulp and paper industry can also be provided.

[0015]When using it in order to manufacture an aerosol which should introduce an aluminium chloride salt dissolved underwater, for example, a silicon dioxide by this invention is obtained as an output, and polar solvents, for example, underwater, can be made to distribute it very easily. Therefore, this silicon dioxide is preferred in order to use it for manufacture of ink jet paper and an ink jet film. It can be used making a thermal decomposition method silicon dioxide which carried out doping processing able to distribute underwater, and transparence or gloss spreading can be applied on an ink jet medium, for example, paper, or a film.

[0016]Next, lessons is taken for a silicon dioxide by this invention, its process, and its use from drawing 1 and the following example, and they are explained further in full detail.

[0017]Drawing 1 is a drawing of a doping system. Main formation parts of this device are the publicly known burners designed for manufacture of a thermal decomposition method oxide.

[0018]The central tube 2 is comprised, this pipe is opened into the nozzle 3, main gas flow flows all over a combustion chamber from here, and the burner 1 burns there. The nozzle 3 is surrounded by the annular nozzle 4 and hydrogen flows from here (circulation or secondary).

[0019]The axial flow pipe 5 is located in the central tube 2, and has finished this axial flow pipe several centimeters before a nozzle of the central tube 2. An aerosol is introduced into the axial flow pipe 5.

[0020]Although an aerosol comprises aluminium chloride solution, it is manufactured in the aerosol generator 6 (ultrasonic atomizer).

[0021]It lets inside of the heating-zone region 7 pass using a mild carrier gas style, company water evaporates there, and the aluminium chloride / water aerosol manufactured in the aerosol generator 6 remain in a form where the Koshio crystal was minutely distributed in a gas phase.
[0022]
[Example]Manufacture $AlCl_4$5.25kg of a thermal decomposition method silicon dioxide (it has low BET surface area)/o'clock which doped the aluminum oxide using example 1 aerosol is evaporated at about 130 **, and it moves into the central tube 2 of the burner 1. Next, the time of 3.47 Nm of hydrogen (primary) ^{3}/and 3.76 Nm of air ^{3}/is introduced into the central tube 2. The time of 0.95 Nm of oxygen ^{3}/is added to this mixture.
[0023]A gaseous mixture flows from the nozzle 3 of the burner 1, and burns in the flame pipe linked to a combustion chamber and this which carried out water cooling.
[0024](A jacket or secondary) The time of 0.5 Nm of hydrogen ^{3}/and 0.3 Nm of nitrogen ^{3}/is introduced into the annular nozzle 4.
[0025]It introduces all over a combustion chamber also at the time of 20 Nm of air ^{3}/(secondary).
[0026]Secondary gas flow flows into the central tube 2 from the axial flow pipe 5.
[0027]Secondary gas flow comprises an aerosol and this is manufactured by the ultrasonic atomization of an $AlCl_3$ solution in the aerosol generator 6. In that case, the aerosol generator 6 sprays 460g/o'clock of aluminum trichloride solution 2.29%. An aluminium chloride aerosol has a heating tube way let it pass with the help of [at the time of 0.5 Nm of air ^{3}/as carrier gas], and an aquosity aerosol changes to a gas and a salt crystal aerosol at the temperature of about 180 ** in that case.
[0028]The temperature of a gaseous mixture ($AlCl_4$ / air / hydrogen, water aerosol) is 156 ** in a burner opening part.
[0029]The thermal decomposition method silicon dioxide which doped the aluminum oxide using reaction gas and an aerosol is taken out through a cooling system by application of decompression. A particle/gas flow is cooled by about 100-160 ** as the result. It flows out and a solid is separated from gas flow in a cyclone.
[0030]The thermal decomposition method silicon dioxide which doped the aluminum oxide using the aerosol is obtained as white detailed powder.
[0031]At the following process, it removes from a silicon dioxide by processing the chloride residue which has adhered by an air content style, raising temperature.
[0032]The BET surface area of the thermal decomposition method silicon dioxide which doped the aluminum oxide is $55m^2$/g.
[0033]Manufacturing conditions are summarized in Table 1. Table 2 expresses the analytical data of others of the silicon dioxide by this invention.
[0034]Manufacture $AiCl_4$4.44kg of a thermal decomposition method silicon dioxide (it has low BET surface area)/o'clock which doped the aluminum oxide using example 2 aerosol is evaporated at about 130 **, and it moves into the central tube 2 of the burner 1 of a publicly known design. The time of 3.15 Nm of hydrogen ^{3}/and 8.2 Nm of air ^{3}/is introduced into the central tube 2 (primary).
[0035]A gaseous mixture flows out of the nozzle 3 of the burner 1, and burns in the flame pipe linked to a combustion chamber and this which carried out water cooling.
[0036](A jacket or secondary) The time of 0.5 Nm of hydrogen ^{3}/and 0.3 Nm of nitrogen ^{3}/is introduced into the annular nozzle 4.

[0037]It introduces all over a combustion chamber additionally also at the time of 12 Nm of air ^{3}/(secondary).
[0038]The second gas flow flows into the central tube 2 from the axial flow pipe 5.
[0039]The second gas flow comprises an aerosol and this is manufactured by the ultrasonic atomization of an $AlCl_3$ solution in another atomiser 6. In that case, 450g/o'clock of aluminum trichloride solution is sprayed 2.29% by the aerosol generator 6. An aluminium chloride aerosol has a heating tube way let it pass with the help of [at the time of 0.5 Nm of air ^{3}/as carrier gas], and an aquosity aerosol changes to a gas and a salt crystal aerosol at the temperature of about 180 ** in that case.
[0040]The temperature of a gaseous mixture ($AlCl_4$ / air / hydrogen, water aerosol) is 180 ** in the opening of a burner.
[0041]The thermal decomposition method silicon dioxide which doped the aluminum oxide using reaction gas and an aerosol is taken out through a cooling system by application of decompression. A particle/gas flow is cooled by about 100-160 ** as the result. It flows out and a solid is separated from gas flow in a cyclone.
[0042]The thermal decomposition method silicon dioxide which doped the aluminum oxide using the aerosol is obtained as white detailed powder. At the following process, it removes from a silicon dioxide by processing the chloride residue which has adhered by an air content style, raising temperature.
[0043]The BET surface area of the thermal decomposition method silicon dioxide which doped the aluminum oxide is 203m^2/g.
[0044]Table 1 expresses manufacturing conditions. Table 2 expresses the analytical data of others of the silicon dioxide by this invention.
[0045]The experimental condition of manufacture of the thermal decomposition method silicon dioxide which doped the 1st table aluminum oxide [0046]
[Table 1]

No.	$SiCl_4$ kg / h	一次空気 Nm^3/ h	O_2 centre Nm^3/ h	Sec. air Nm^3/ h	H_2 centre Nm^3/ h	H_2 ジャケット Nm^3/ h	N_2 ジャケット Nm^3/ h	気体温度 ℃	塩溶液	エーロゾル量 kg / h	Air aeros. Nm^3/ h	BET m^2/g
1	5.25	3.76	0.95	20	3.47	0.5	0.3	156	2.29% 水溶液 $AlCl_3$	0.46	0.5	55
2	4.44	8.2	0	12	3.15	0.5	0.3	180	2.29% 水溶液 $AlCl_3$	0.45	0.5	203

[0047]legend: -- primary air = -- quantity [of the air in a central tube]; -- Sec.air= secondary air; -- hydrogen [in an H2centre= central tube]; -- gas temperature; in the nozzle of a gas temperature = central tube -- amount of aerosols = -- mainstream **; of the salting in liquid which changed to the aerosol form -- Air. The amount of carrier gas (air) of an aeros.= aerosol;
Analytical data of the sample obtained by the examples 1-2 of the 2nd table [0048]
[Table 2]

	BET m^2/g	pH 値 4% susp.	スタンピング密度 g/l	DBP 吸収 g/100 g	Al_2O_3 含量 質量%	SiO_2 含量 質量%	塩化物含量 ppm		
実施例 1	55	4.39	94	81	0.187	99.79	89		
実施例 2	203	4.15	24	326	0.27	99.67			
比較例									
Aerosil OX 50	50	3.8 ～ 4.8	130	約 160	<0.08	>99.8	<250		

[0049]legend; -- pH value electron microscope photograph [of pH4%susp.=4% aqueous suspension]: -- drawing 2 expresses the electron microscope photograph of the thermal decomposition method silicon dioxide which doped the aluminum oxide using the aerosol by Example 1.
[0050]Many simple independent spherical primary particles characterize existing.
[0051]Especially the difference with the thermal decomposition method silicon dioxide which doped the aluminum oxide using the aerosol of this invention, and the thermal decomposition method silicon dioxide which has the same criticism area manufactured using the publicly known method is expressed by the DBP absorption which is a measure of the "structure" (namely, grade of connate) of a thermal decomposition method silicon dioxide.
[0052]Namely, although silicon dioxide OX50 of marketing manufactured using the pyrolysis high temperature flame hydrolysis method shows DBP absorption of about 160 (g/100g) (with BET surface area ^{2}[of 50 m]/g), On the other hand, the thermal decomposition method silicon dioxide which doped $aluminum_2O_3$0.187 mass % by this invention shows the DBP absorption which is only 81 (g/100g). Very low DEP absorption means that low viscous suspension can be manufactured from the thermal decomposition method silicon dioxide which doped the aluminum oxide of this invention. With these characteristics, the suspension which has a charge content of high restoration can be manufactured easily.
[0053]The dispersibility and homogeneous-mixing nature which were excellent in the silicon dioxide by this invention deserve special mention.
[0054]Especially this is advantageous in order to use it as an absorptivity loading material by paper making also including the use in ink jet paper and an ink jet film.
[0055]Transparence and gloss spreading can also be manufactured from the dispersion liquid of the silicon dioxide by this invention.
[0056]Table 3 expresses a difference of a uniform miscibility action and viscosity.
[0057]The thermal decomposition method oxide and mixed oxide of the following marketing are used for comparison (altogether). [Degussa and] They are certain :Aerosil 200 (thermal decomposition method silicon dioxide), MOX170 (the aluminum / silicon mixed oxide manufactured with the thermal decomposition method), and Aluminiumoxid C (aluminum oxide manufactured with the thermal decomposition method) with the product of Frankfurt **.
[0058]
[Table 3]

名 称	Aerosil A 200	MOX 170	Alu C	実施例 1	実施例 2
SiO_2 含量 [質量%]	>99.8	>98.3	<0.1	99.79	99.67
Al_2O_3 [質量%]	<0.05	0.8	>99.6	0.187	0.27
BET [m^2/g]	200	170	100	55	203
DBP 吸収 [g/100 g]	330	332	230	81	325
均一混和性 [--]	不良~普通	普通	普通	非常に良好	普通
粘度 [mPas]					
5 rpm で	4560	880	560	400	14480
100 rpmで	1200	420	330	210	2570
BET					
焼結前	200	170		55	203
1150℃で 3 時間 焼結後	17	43		50	125
[m^2/g]					
嵩密度 焼結前	40	40		73	17
1150℃で 3 時間 焼結後	160	220		80	26
[g/l]					

[0059]Homogeneous-mixing nature is related with the speed by which churning mixing of the powder is carried out into an applicable fluid.

[0060]Silicon dioxide >98.3 mass % and aluminum$_2O_3$0.8 mass % are contained, As compared with mixed oxide MOX170 which was manufactured by the flame hydrolysis of the mixture of aluminum$_2Cl_3$ and $SiCl_4$ and which was manufactured with the publicly known thermal decomposition method, the thermal decomposition method silicon dioxide doped using the aerosol by this invention shows the sintering activity which decreased remarkably.

[0061]A publicly known thermal decomposition method oxide (silicon dioxide), for example, Aerosil 200, and MOX170 (aluminum$_2O_3$/SiO_2 mixed oxide) are sintered with the remarkable increase in bulk density, and BET surface area decreases rapidly simultaneously in that case so that clearly from Table 3.

[0062]Contrary to this, the thermal decomposition method silicon dioxide doped using the aerosol of this invention only produces change of very slight bulk density after sintering. This means that the silicon dioxide by this invention has the sintering activity which decreased remarkably.

[0063]Viscosity was measured in the aquosity dispersion liquid of 15% of solid content. :thermal decomposition method silicon dioxide 50 mass part, Mowiol 28 - 29 (polyvinyl alcohol, Cassella-Hoechst) 30 mass part, and Lumiten PPR8450 (polyvinyl-pyrrolidone, BASF) 50 mass part to which solid content changes from the following mass part in that case.

[0064]Aqueous suspension is agitated for 30 minutes at 3000 rpm in a high speed stirrer 15%, and subsequently it is neglected for 24 hours, and then agitates by the short time and a hand, and the size of a spindle is measured with a Brookfield viscometer (RVT type) according to each viscosity at 23 **.

[0065]Evaluation of a printing action : A commercial film (Kimoto 105 g/m^2) is applied using the No. 4 spreading knife with these 15% dispersion liquid saved for ten days (since short-time shake is carried out), It prints using a Hewlett Packard (Hewlett-Packard) 550C printing machine. Vision evaluation of the printing quality is carried out (peak price =1, minimum value =6).

[0066]Table 4 and 5 expresses the result of three color prints and four color prints.

[0067]4th Table: Three Color Print (All Colour) HP550C [0068]

[Table 4]

名 称	Aerosil A 200	MOX 170	Alu C	実施例 1	実施例 2
色強度					
M/G /C	1	1	1	1	1
黒	1	1	1	1	1.75
ドット鮮鋭度					
色中黒	1.5	1.75	1.75	1.75	1.5
転移					
色中色	1	1	1	1	1
ドット鮮鋭度					
黒色印刷	1	1	1	1	1.75
ドット鮮鋭度					
黒色輪郭	1.5	1.5	1	1	1.5
連続色調印刷					
色強度 / 輪郭	1	1	1.75	1.5	1
総合評価	8	8.25	8.5	8.25	8.5
平均評価	1.14	1.17	1.21	1.17	1.21

[0069]M/G/C: Magenta, green, 5th table [of cyanogen]:4 color print (Black and Colour) HP550C[0070]

[Table 5]

名称	Aerosil A 200	MOX 170	Alu C	実施例 1	実施例 2
色強度 M/G /C 黒	1 1	1 1	1 1	1 1	1 1
ドット鮮鋭度 色中黒	3.5	3.5	1.5	3	3.5
転移 色中色	1	1	1	1	1
ドット鮮鋭度 黒色印刷	1	1	1	1	1
ドット鮮鋭度 黒色暗部	1.5	1.75	1.75	2	1.75
連続色調印刷 色強度／輪郭	1.5	1.5	1.5	1.5	1.5
総合評価	10.5	10.75	9.5	10.5	9.75
平均評価	1.5	1.5	1.4	1.5	1.4

[0071]As a principle, combination into the loading material of others in ordinary use or its mixture is also possible at the thermal decomposition method silicon dioxide, the sedimentation method silicon dioxide, the bentonite, or the pulp and paper industry of the silicon dioxide wave of this invention, and others.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]In a thermal decomposition method silicon dioxide which doped an aluminum oxide using an aerosol, It is the silicon dioxide which a basic component manufactured with a thermal decomposition method using a flame oxidation style or flame hydrolysis, The ingredient is doped by a doping component to $1x10^{-4}$ and 20 mass %, In that case, doping quantity is 1-10000 ppm, and a doping component, They are a salt of aluminum, a salt mixture, an aluminium compound, suspension of metallic aluminum, or its mixture, A thermal decomposition method silicon dioxide which doped an aluminum oxide using an aerosol, wherein BET surface area of a doped oxide is 5-600m^2/g.

[Claim 2]In manufacturing a thermal decomposition method silicon dioxide which doped an aluminum oxide using an aerosol, so that it may be used for a thermal decomposition method silicon dioxide by a flame oxidation style or flame hydrolysis, Introduce an aerosol into a flame, and before reacting an aerosol, it mixes with flame oxidation or a flame hydrolysis gaseous mixture to homogeneity, Subsequently, a thermal decomposition method silicon dioxide which the aerosol/gaseous mixture was made to react in a flame, and was produced and which doped an aluminum oxide is separated from gas flow by a publicly known method, It manufactures using solution which is the form dissolved or suspended [aerosol] in a salt, a salt mixture, or the metal itself of aluminum, or contains the mixture in that case, A process of a thermal decomposition method silicon dioxide which doped an aluminum oxide using the aerosol according to claim 1 manufacturing by spraying using 2 liquid nozzle of an aerosol, or manufacturing as directed under [aerosol] other in that case.

Drawing selection Drawing 2

[Translation done.]